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AND OXYGEN IN SOLUTIONS TO MOLECULAR STRUCTURES

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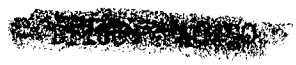
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THE RELATIONSHIP OF THE ISOTOPE EXCHANGE OF HYDROGEN  
AND OXYGEN IN SOLUTIONS TO MOLECULAR STRUCTURES

Following is the translation of an article  
entitled "Zavisimost' Isotopnogo obmena Vodoroda  
i Kisloroda v Rastvorakh ot Stroyeniya Molekyl  
(English Version Above) in Voprosy Khimicheskoy  
Kinetiki Kataliza i Reaktsionnoy Sposobnosti  
(Problems of Chemical Kinetics of Catalysis  
and Reaction Capability), Moscow, 1955, pages  
18-23.

HYDROGEN EXCHANGE

1

According to the doctrine of A. M. Butlerov, the properties of molecules are determined not only by the number, nature, and order of the atom combinations but also by their mutual effect. Therefore, extrapolation of properties which are imparted by abstract (isolated) bonds to the properties of the same bonds in molecules represents only a crude approximation, which in many cases leads to a contradiction of experience.

Simple and characteristic examples of the strong influence of structure on the behavior of atoms with similar bonds but in different molecules can be found in data dealing with the velocity of hydrogen isotope exchange. These examples are of interest because, in them, the deciding role is played not by the displacement of electron shells under the influence of the neighboring atoms and groups (effects of induction and linkage), which are preferentially studied in contemporary theory of organic chemistry - but by the qualitative differences connected with the participation of these shells in the formation of different valency bonds.

In N - H, O - H, S - H, Cl - H bonds and in other bonds in the majority of compounds studied so far, the exchange of hydrogen to deuterium of the polar donors (for example, D<sub>2</sub>O) is carried out with immeasurable speed.

It is accepted that this kinetic exchange is typical for the noted bonds in any molecules in contrast to the exchange in C-H bonds which is possible and proceeds at a speed admitting observation, only if the bond is ruptured or activated by the corresponding substitutes or catalyzers.

However, it is known that in a series of aminocomplexes, in ammonium diboron, and in  $\text{BH}_4^-$ , the exchange in the N-H and B-H bonds progresses slowly; that in the H-H bond of molecular hydrogen it proceeds only in the presence of catalyzers, ortho-para-conversion, and so forth. On the other hand, it is impossible to find a single physical characteristic of the C-H bond which could explain its position relative to hydrogen exchange. In 1949, the author /1, 8/ expressed a theory stating that the velocity of the hydrogen exchange in the X-H bond substantially depends not so much on the nature of the atom X as on the bonds between the electrons in its shell and the adjoining atoms. If in this shell there exists a pair of free electrons, then the proton (or, correspondingly, deuteron) may attach itself to it with the simultaneous breaking away of the other proton (deuteron) from the other electron pair of this shell in a single elementary act. This leads to an exchange, the activating energy of which can be estimated at 2-3 kcal/mole by analogy with a similar process of proton transition in the mechanism of electroconductivity according to Grotgoss. Such an exchange must proceed very rapidly even at low temperature. In organic compounds, free electron pairs do not exist in proximity to the hydrogen atom in C-H bonds and the attachment of a proton (deuteron) requires a rupture of the C-H bond at the same elementary act or before it; only after this may there form a new C-H or C-D valence bond. This process obviously demands considerable activating energy and the exchange either does not proceed or is more or less retarded.

The first type of exchange was conditionally designated as fast and the second as slow. This, of course, does not exclude the possibility that in separate cases the exchange according to the slow mechanism is capable of proceeding fairly rapidly. An essential classification feature for both exchange mechanisms is the effect of substitutes and catalyzers, which play a deciding role in the mechanisms of slow exchange but which are non-essential (at least, according to the contemporary level of kinetic study of very fast reactions) for a mechanism of rapid exchange.

In order to substantiate this theory, my coworkers, L. V. Sulima and I. G. Khaskin, arranged several experiments. It was found that in contrast to ammonia, in the ion of ammonium, where free electron pairs do not exist near the atom of nitrogen, the exchange proceeds with a measurable velocity and decelerates even more in the presence of acids. We explained this by the fact that the exchange proceeds not in the  $\text{NH}_4^+$  itself but in ammonia, which exists in hydrolytic equilibrium, so that the exchange

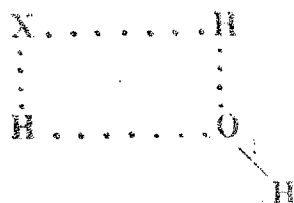
velocity is determined by the speed of the hydrolysis. In bonds P-H of phosphorous acid and its anion, the exchange does not proceed at all, because there are no free pairs of electrons near the atom of phosphorus. The exchange proceeds relatively fast in the same bonds of hypophosphoric acid as a result of tautomeric regrouping  $\text{H}_2\text{P}(\text{O})(\text{OH}) = \text{HP}(\text{OH})_2$ , during which an electron pair is liberated near the atom of phosphorus. This method of exchange was substantiated by comparing its kinetics with the kinetics of the oxidation of  $\text{H}_3\text{PO}_2$ , which proceeds through the stage of tautomeric transition. In Si-H bonds of trisilane, where again there is no free pairs of electrons in proximity to the atom of silicon, exchange was not discovered even under most drastic conditions.

To the cited data, it is necessary to add that at the present time there is not a single authentic case known in which the exchange in X-H bonds in a solution of donor deuterium did not proceed with immeasurable speed if the shell of the X atom contained free pair of electrons. Also, there is not a single case known in which - with the absence of such pair - the exchange was more or less fast in the absence of conditions highly activating the X-H bond. In C-H bonds of hydrocarbons, examples of most rapid exchange were found in the medium of liquid  $\text{ND}_3 + \text{ND}_2$  due to the strong basicity of the medium, but in these specially favorable conditions the exchange proceeded with a measurable speed /2/.

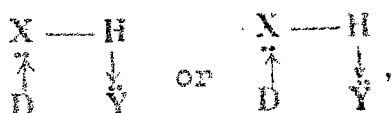
## 2

The rapid hydrogen exchange in N-H, O-H and S-H bonds and in others in dissolved compounds is usually attributed to their electrolytic dissociation. For example, in solutions of heavy water, the free ions  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  of solute are replaced by the same kind of ions,  $\text{D}_3\text{O}^+$  or  $\text{OD}^-$ , from the water. Electrolytic dissociation, similar to the exchange reaction of the above-mentioned bonds, actually proceeds immeasurably fast. More careful examination of the question leads, however, to the conclusion that, in the mechanism of fast exchange, electrolytic dissociation does not play a deciding role. It is possible to cite many examples of practically instantaneous exchange when the equilibrium concentration of the free ions participating in it has a value of  $10^{-14}$  order of less, which is insufficient for such a fast exchange. It would be more correct to consider that the exchange according to the fast mechanism and electrolytic

dissociation are two parallel processes the second of which, of course, also leads to an exchange, but slower than the first. Indeed, dissociation apparently proceeds through a stage of an intermediate complex type:



(for an example of an acid dissociation in water) with polarizing (in particular, the hydrogen type) bonds. The rupture in such complexes on  $X^- + H_2O^+$  or on  $HXH^+ + OH^-$ , obviously, demands considerably greater energy of activation than the symmetrical process of transition of two protons to free electron pairs in a complex:



and this presents, as was pointed above, characteristic peculiarity of the rapid exchange mechanism. In the absence of free electron pairs near the X or D atoms, the energy of activation must be high because in the corresponding intermediate complex the weak polarizing bonds X-D and Y-H may be transferred into valence bonds only through a process of freeing electron pairs from the original valence bonds X-H and Y-D. This process may proceed slower than the electrolytic dissociation. Therefore, the exchange according to the mechanism of slow exchange may proceed either in a single act (this is usually called an association mechanism) or through a preliminary step of electrolytic dissociation (ionizing exchange mechanism).

The examined consideration can be extended to other protolytic reactions. They apparently explain the very small acidity of hydrocarbons. The absence of free pairs of electrons near the atoms of carbon in C-H bonds; the small inclination of these atoms toward coordinated joining and toward participation in hydrogen bonds -- all this hinders the formation of corresponding intermediate complexes.

During the mechanism of slow exchange -- contrary to the mechanism of fast exchange -- the deciding effect on the velocity is exerted by factors weakening the original X-H bonds. The most important of these factors are: a great

difference in the acidity of both participants of the exchange, suitable substitutes, and the junction of the bonds. The first is manifested by sensitivity of the exchange toward the acid-base catalysis and, in particular, in sharp change in the exchange velocity during the transition from  $D_2O$  in liquid  $ND_3$  or  $DBr$ , as was shown in recent broad-scale investigations by A. I. Shatenshteyn /3/. The effect of substitutes is well known in many examples of organic-compounds exchange. As for effects of linkage in hydrogen exchange, the linkage  $\sigma-\pi$  has the greatest effect (because the X-H bond is a  $\sigma$  bond), as was established by A. N. Nesmeyanov /4/ and experimentally substantiated by works of A. N. Nesmeyanov, D. N. Kursanov /5/, A. I. Shatenshteyn /3/ and G. F. Maklukhin /6/.

Here we are not examining the radical exchange mechanism in solutions connected with the homologous rupture of bonds, inasmuch as the material on hand is insufficient for generalized conclusions.

#### OXYGEN EXCHANGE.

1

The exchange of oxygen isotopes in a solution differs considerably from the exchange of hydrogen. It almost always proceeds slowly and strongly and depends on the acidity or basicity of the medium. The selection of the objects and conditions in connection with its study has been for the most part of a casual character and the experimental results of various authors have been completely contradictory. All this hinders obtaining generalized conclusions with reference to oxygen exchange.

From the many variants of oxygen exchange, the most important appear to be the following:

a) An exchange in anions through formation of free acids or their anhydrides, for example:



In this manner, various authors explained the exchange in  $HSO_4^-$ ,  $HSO_3^-$ ,  $CrO_4^{2-}$ ,  $Cr_2O_7^{2-}$ ,  $ClO_4^-$ ,  $ClO_3^-$ ,  $HCO_3^-$ ,  $CO_3^{2-}$  and so forth. However, some of the substances also exchange oxygen in an alkaline medium, for which the noted mechanism is unsuitable. The more so as it does not agree with the occasionally observed alkaline catalyses (bichromates, silicates, and so forth).

b) An exchange through an addition - subtraction of the hydroxyl is the method sometimes offered for explaining

the exchange in carbonyl complexes under the conditions of alkali-catalysis. This mechanism has only limited circulation. It explains neither the exchange in the acid medium, nor - even more so - the often observed organic anions of the acid catalysis /8/.

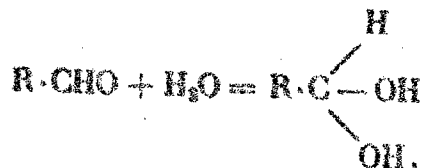
c) An exchange through ionization, either immediately or after intermediate junction of the proton. Such a mechanism, of course, fully explains the exchange of hydroxyl groups of strong bases with water, but it is found with difficulty and requires artificial supplementary allowances in other cases.

d) An exchange through hydrolysis, for example:



An exchange in  $\text{BO}_3^{2-}$ ,  $\text{B}_4\text{O}_7^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{Cr}_2\text{O}_7^{2-}$  and others was explained in this manner. Undoubtedly, this mechanism deserves attention, particularly for anions of weak acids, where it is entirely probable. In a series of cases, however, it does not agree with the characteristic effect and bases on the velocity of the exchange and with the disruption of the relationship between the exchange velocity and the acid strength.

e) An exchange through addition of water with formation of the ortho - form, for example:



Such a mechanism explains satisfactorily the exchange in carbonyl of organic compounds and agrees with the known chemical properties of this group. We made no attempt to explain other cases related to it. We will return to this mechanism later.

f) We made an attempt to characterize the aptitude toward the oxygen exchange and its velocity by means of the polarity degree of the X-O group; it takes place /7/, but an objective comparison with the known experimental facts substantiates this point of view only to a slight degree.

Comparison of the available but as yet scarce material with reference to oxygen exchange in solutions does not disclose a simple connection with the nature of the exchange compounds. As will be disclosed further, some success in this direction can be achieved by considering individual structures of the electron shells in solvents.

Comparison of the velocity of the oxygen exchange in acids of phosphorus and their salts in work of L. V. Sulima and the author /9/ gives a series (in brackets - the half period of the exchange in hours and the temperature of the experiment):

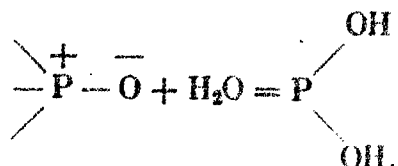
$\text{H}_3\text{PO}_2 (< 0,2; 40^\circ) > \text{H}_3\text{PO}_3 (6,5; 63^\circ) > \text{H}_3\text{PO}_4 (70; 100^\circ)$   
and for anions

$\text{H}_2\text{PO}_2^- (10; 100^\circ) > \text{HPO}_3^{2-}, \text{H}_2\text{PO}_4^-, \text{HPO}_4^{2-}, \text{PO}_4^{3-} (0; 100^\circ).$

All three acids possess a single structure

$\text{H}_3\text{P}(\text{O})(\text{OH}), \text{HP}(\text{O})(\text{OH})_2$  and  $\text{P}(\text{O})(\text{OH})_3$ ,

so that in this series is clearly disclosed the retardation of the exchange with the increase of the hydroxyl groups connected with phosphorus and also at the transition of the acid to its anion\*. The found relationships can be satisfactorily explained by a mechanism usually accepted for the explanation of the exchange in the carbonyl group: an intermediate annexation of water according to a formal double bond  $\text{P}=\text{O}$



An increase in the number of hydroxyl groups, connected with phosphorus, decreases the positive charge in the latter and its ability to nucleophilic annexation of the water hydroxyl. In the same direction, and even to a greater degree, act the free negative charges on the oxygen atoms in anions.

From the fragmentary experimental material which is available today, it is possible to arrive at the same conclusions for other cases of oxygen exchange. This exchange proceeds with ease in concentrated  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$  (where

\*More rapid exchange in solution of a partially dissociated acid can not be attributed to acid catalysis in the anion, inasmuch as such a catalysis was not disclosed in the solutions of these salts. Also, in the same solutions, no basic catalysis was ever disclosed.



undissociated molecules predominate) and in solutions of weak acids  $H_2SO_3$ ,  $H_2CO_3$ ) but much slower in the diluted solutions of the first; in acid anions  $HSO_4^-$ ,  $HSO_3^-$ ,  $HCO_3^-$  and even slower in  $SO_4^{2-}$ ,  $SO_3^{2-}$ ,  $NO_3^-$  and  $CO_3^{2-}$ . Slow exchange is observed in carbonaceous acids but not in their salts. The same mechanism explains the absence of exchange in hydroxyl groups of alcohols and single substitutions phenols.

### 3

We have no intention of applying the examined mechanism to all cases of oxygen exchange. It is only possible if the central atom possesses the ability of coordinated attraction while the number of electrons in its shell is increasing. For instance, the absence of a noticeable exchange in perchlorates should be attributed to the inability of chlorine to expand its shell in excess of eight. In periodides, where such expansion is possible (for instance,  $H_5JO_6$ ) the exchange proceeds exceedingly fast, as was demonstrated recently by N. A. Vysotskaya.

On the other hand, this mechanism requires considerable polarization of the X-O bond for migration of electrons to the oxygen atom. The degree of such polarization must be able - as was noted above - to strongly influence the velocity of the exchange. It must depend on substitutes, and on the linkage  $\sigma$ - $\pi$  in the chain  $A \rightarrow B \rightarrow X \rightarrow O$

which in turn depends on the polarity of the group X-O /4/. The polarity of the latter, obviously, is responsible for the effect of the hydroxyl groups in the exchange of acids of phosphorus, where the P-O bond shows a binary character.

Further investigations will disclose how extensively the proposed mechanism of oxygen exchange occurs., but from the data on hand it is possible to conclude that it is closely connected with the structure of electron shells in molecules.

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